Supplementary Information for:

Sorption and photodegradation under visible light irradiation of an organic pollutant by a heterogeneous UiO-67-Ru-Ti MOF obtained by Post-Synthetic Exchange.

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1. Digestion of MOFs

For ICP analysis 5 mg of the dried material were digested in a mixture of 0.35 mL of H_2SO_4 and 0.115 mL of H_2O_2. This solution was heated at 120°C during 4 hours until the solution was clear. 60 µL were dissolved in 10 mL of an 2% HNO_3/H_2O solution.

2. Synthesis of ligands

2.1 Synthesis of (2,2'-Bipyridine)-5,5'-dicarboxilic acid (bpydc)[2]

5,5'-dimethyl-2,2'-bipyridine (1 g; 5.43 mmol) and $KMnO_4$ (5.60 g; 35.4 mmol) were added into a round bottom flask with 100 mL of distilled water. The solution was heated and stirred at 115°C during 3 hours. After cooling to room temperature, the solution was filtered and further cooled at 0°C. Then, HCl (37%) was slowly added until the apparition of a white precipitate. The solid was filtered and dried in an oven at 40°C overnight (^{1}H NMR (D_2O+NaOD): δ 8.84(dd,2H) 8.18 (dd, 2H) and 7.92 (dd, 2H)) (yield 50%).

2.2 Synthesis of $Ru(bpy)_2Cl_2$

NaCl (0.499 g, 8.5 mmol), sucrose (0.5135 g, 1.5 mmol) and cis-2,2'-Bypiridine (bipdc)(1.311 g, 8.36 mmol) were added to 10 mL of degased H_2O and 3 mL of concentrated HCl (37%). The mixture is heated and kept under reflux and vigorous agitation for 15 min. In different intervals of 15 minutes, $RuCl_3$ anhydrous (0.741 g, 3.57 mmol) and ascorbic acid (0.886 g, 5 mmol) were added to the solution and kept under stirring and heating during another 15 minutes. The solution was cooled at room temperature and a precipitate was separated by filtration. The filtrated solid was placed in a Soxhlet extractor with dichloromethane during 24 hours. The extracted liquid was distilled and the solid obtained was washed with a saturated solution of $NaHCO_3$. The final solid was separated and dried in an oven at 50°C overnight. (^{1}H NMR 400 Mhz, DMSO, 293.15 K): 10.06 (dd, 2H); 8.72 (dd, 2H); 8.56 (dd, 2H); 8.15 (m, 2H); 7.86(m, 2H); 7.77 (m,2H); 7.19 (m, 2H);) (Yield 55%).

2.3 *Synthesis of [Ru(bpy)$_2$(5,5'-dcbpy)]*

The Ru complex was obtained by following a previously reported procedure [3,4]. Ru(bpy)$_2$Cl$_2$ (160 mg, 0.33 mmol) and bpydc (101 mg, 0.41 mmol) were dissolved in 10 mL of H_2O and 10 mL of ethanol. The solution was kept and stirred under an Ar atmosphere. The solution was then refluxed for 12 hours. The solvent was evaporated and the resulting solid was recrystallized in a solution of 3 mL of MeOH and 20 mL of diethyl ether. The precipitate was filtered and left to dry in an oven at 40°C overnight. (1H NMR (D2O): δ 9.00 (d, 2H), 8.88 (m, 4H), 8.53 (d, 2H); 8.24 (m, 4H); 8.01 (s, 2H); 7.86 (d, 2H); 7.80 (d, 2H); 7.60(t, 2H); 7.53(t, 2H)) (Yield 75%).

3. XRF Analysis

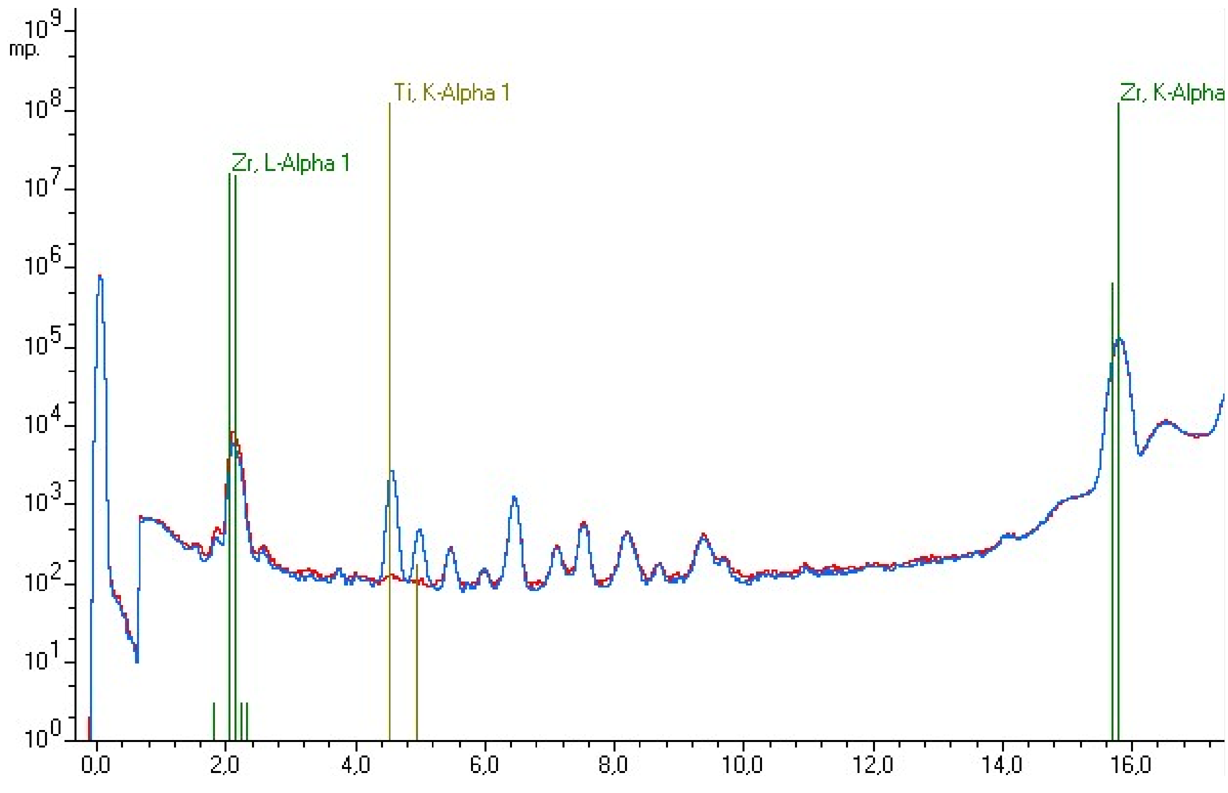


Figure S1. XRF Spectra of UiO-67-Ru and UiO-67-Ru-Ti MOFs

4. Calibration curve for methylene Blue

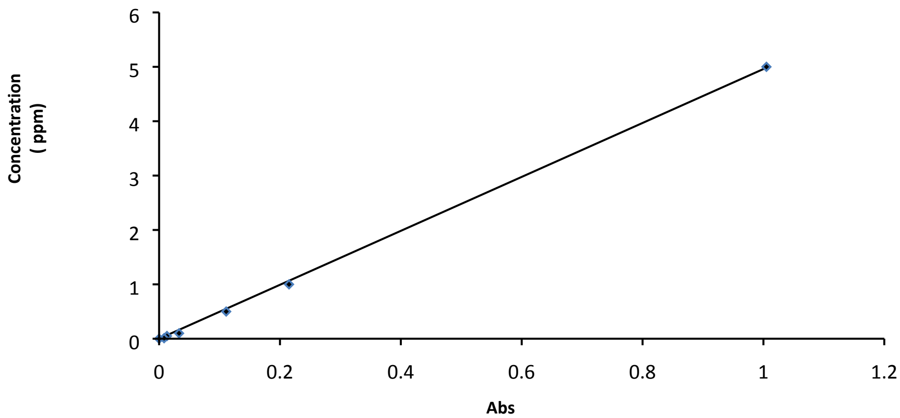


Figure S2. Calibration curve for Methylene Blue

5. Titanium exchange rate

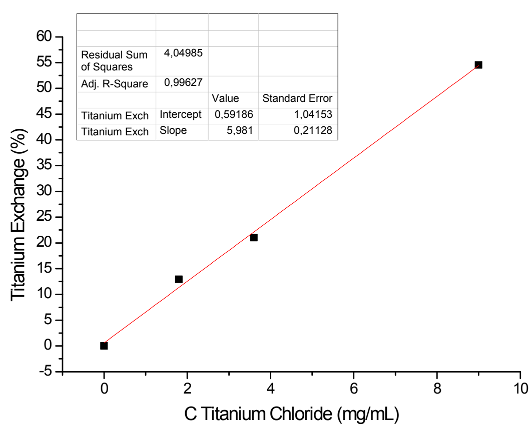


Figure S3. Fitted data for the exchange of Ti in UiO-67 MOFs

6. BET Analysis

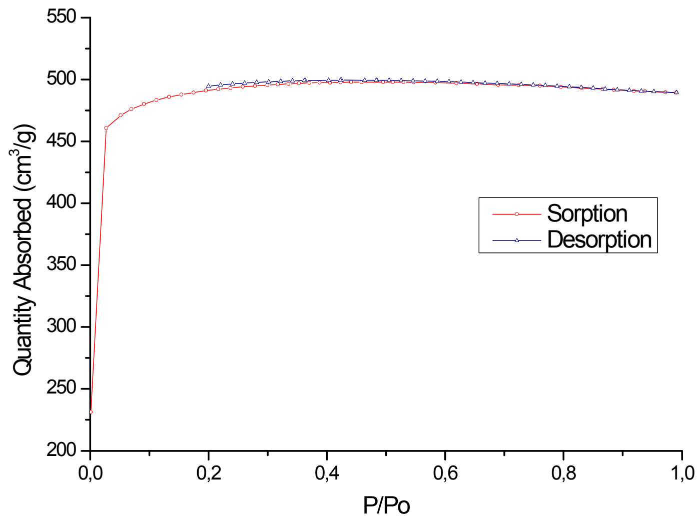


Figure S4. Linear sorption isotherm of UiO-67-Ru

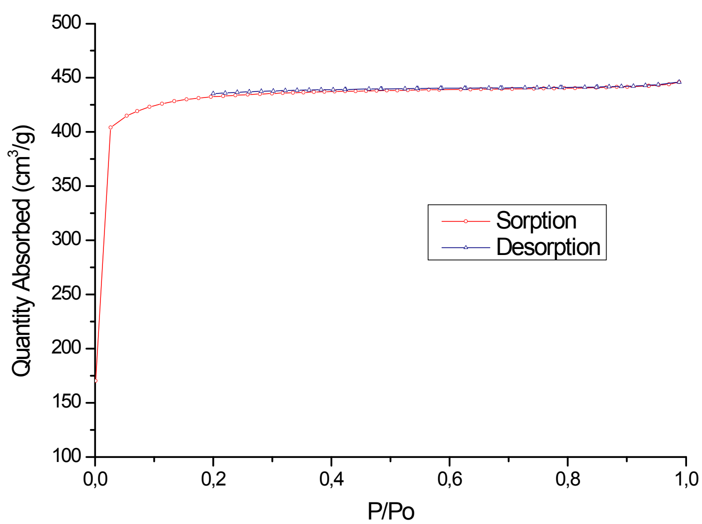


Figure S5. Linear sorption isotherm of UiO-67-Ru-Ti50

7. SEM Pictures

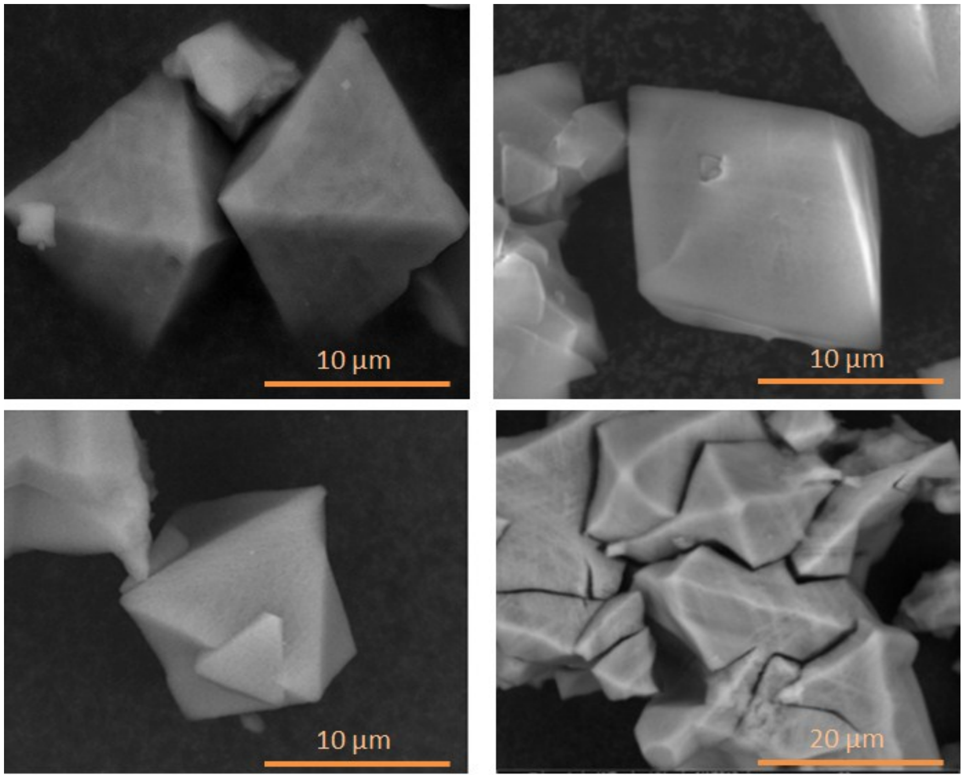


Figure S6. SEM Pictures of differente obtained MOFS a)UiO-67, b)UiO-67-Ti50, c)UiO-67-Ru d)UiO-67-Ru-Ti50

8. Photophysical properties

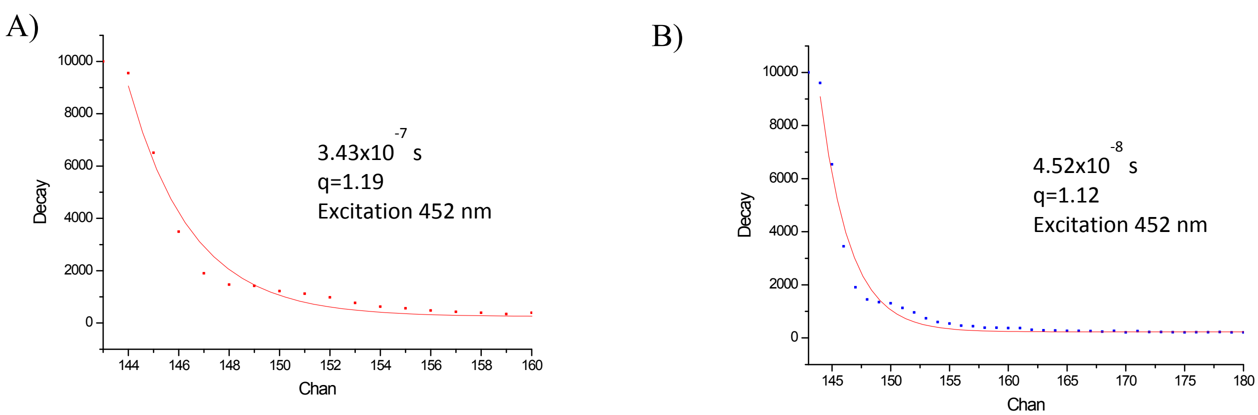


Figure S7. Lifetime of UiO67-Ru (A) and UiO67-Ru-Ti50 (B)

9. Kinetics of the dye sorption

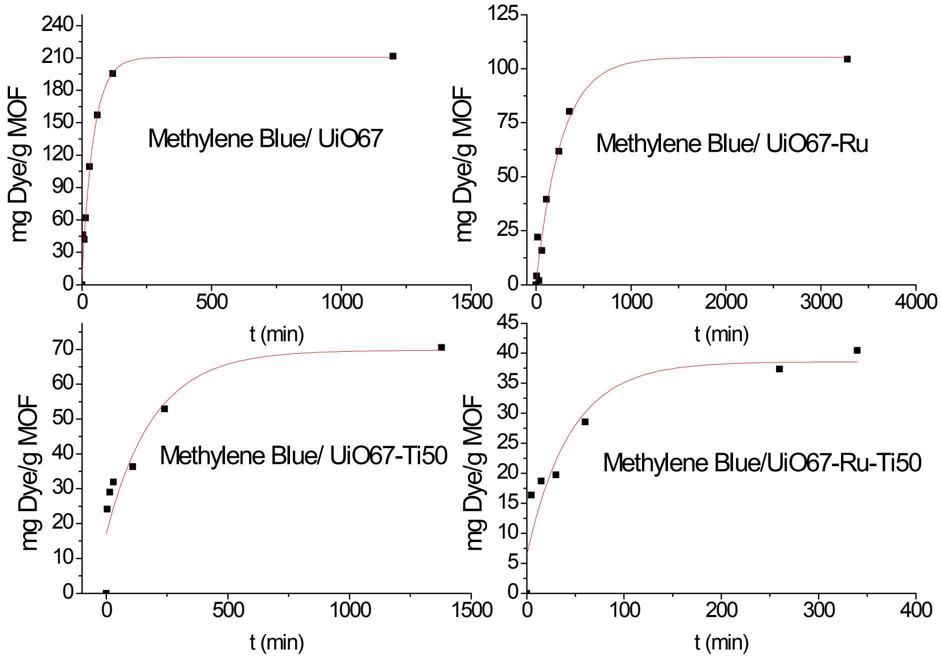
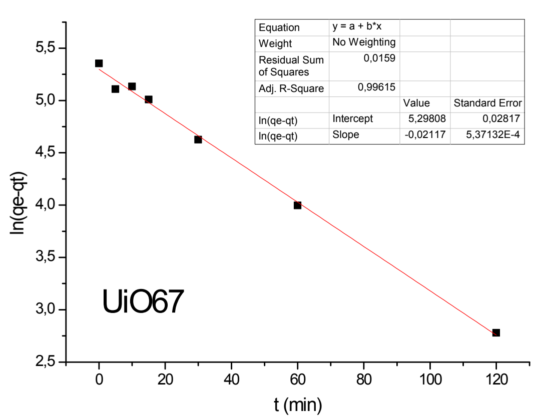
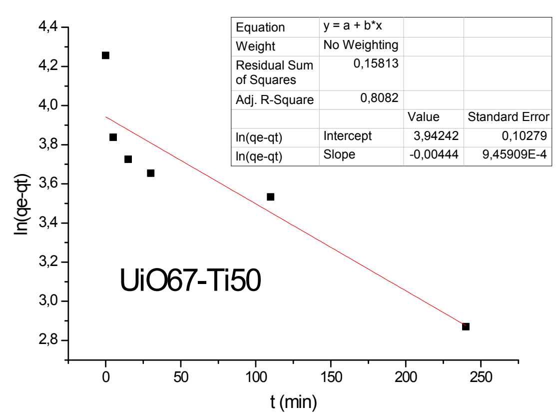


Figure S8. Adsorption isotherms for MB over UiO67, UiO67-Ru, UiO67-Ti and UiO67-Ru-Ti MOFs.





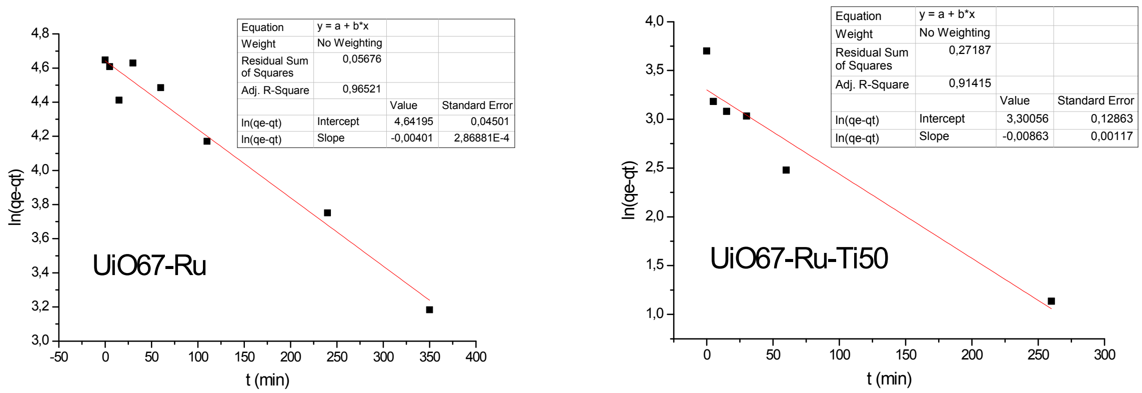


Figure S9. First order fitting adsorption isotherms for Methylene Blue over different MOFs.

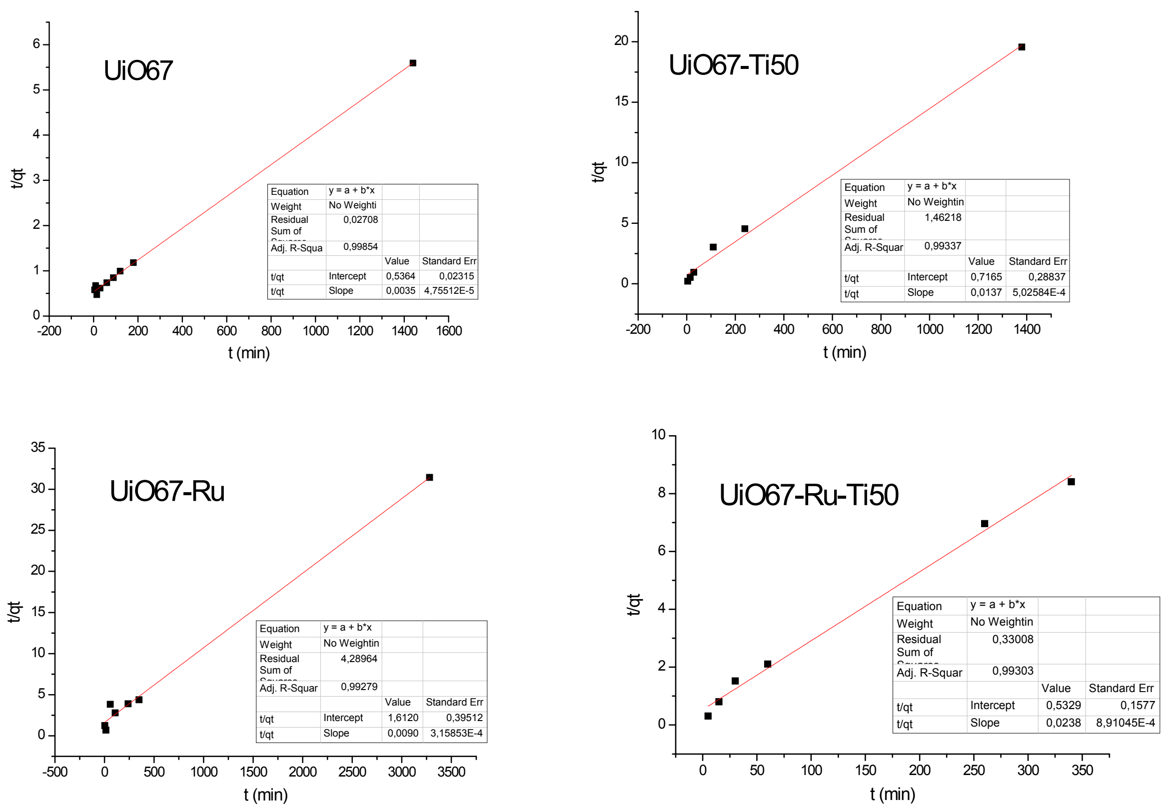


Figure S10. Second order fitting adsorption isotherms for Methylene Blue over different MOFs.

10. Dyes degradation experiments under UV light

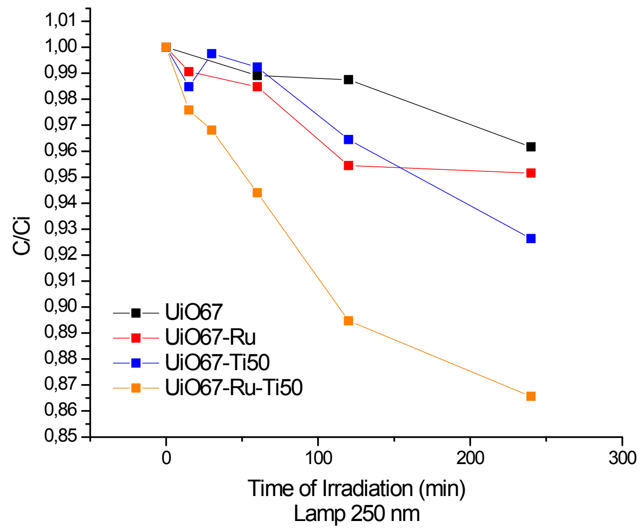


Figure S11. Photo-degradation of MB under UV irradiation (250 nm)

11. Possible degradation products of Methylene Blue

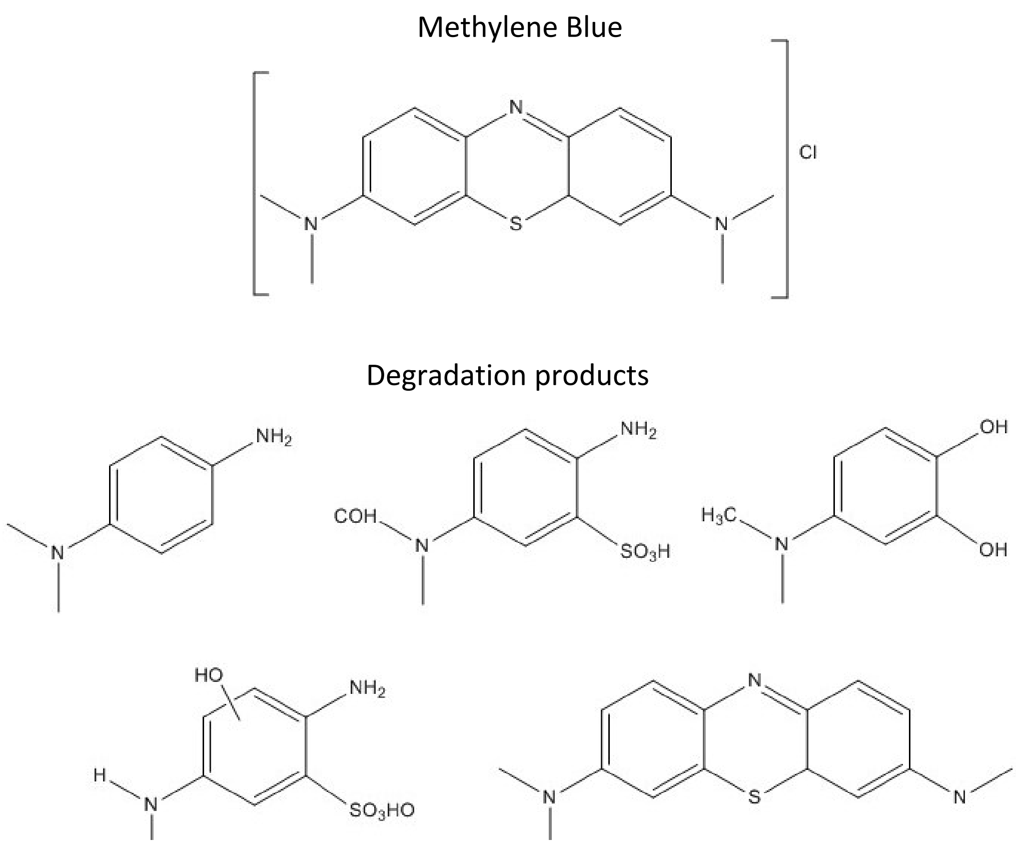


Figure S12. Degradation products of Methylene Blue as studied by Jing et al. [5]

12. Comparison between theoretical and experimental values obtained by TGA

Table S1. Values of theoretical an experimental organic fractions in Ti exchanged and un-exchanged UiO67 MOFs

MOF	Weight % of Inorganic Oxides	Experimental Weight % of Organic Part	Theoretical Weight % of Organic Part
UiO67-Ru	39.18	60.82	66.53
UiO67-Ru-Ti50	47.025	52.98	70.52

13. EDS Analysis (Table)

Table S2. EDS quantification results of UiO-67-Ru-Ti50

Quantification results					
Norm. mass percent (%)					
Spectrum	C	O	Ti	Zr	Ru
Ui067-Ti-Ru 5	24,22812	21,371	7,314645	46,09156	0,994675

14. Kinetic Parameters (Table)

Table S3. Pseudo-first order sorption kinetic parameters for methylene blue on different MOFs

Parameter	*UiO-67*	*UiO-67-Ru*	*UiO-67-Ti50*	*UiO-67-Ru-Ti50*
q_e (exp) (mg/g)	211.49	104.39	70.54	40.46
k_1 [mg/(g min)]	-2.18×10^{-2} ±2.11x10-4	-4.44×10^{-3} ±2.87x10-4	-4.01×10^{-3} ±9.46x10-4	-8.63×10^{-3} ±0.00117
q_e (calc) (mg/g)	199.94±1.03	103.65±1.05	51.54±1.11	27.13±1.14
R^2	0.99	0.96	0.81	0.91

15. References

[1] S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *60*, 309–319.

[2] I. Gamba, I. Salvadó, G. Rama, M. Bertazzon, M. I. Sánchez, V. M. Sánchez-Pedregal, J. Martínez-Costas, R. F. Brissos, P. Gamez, J. L. Mascareñas, et al., *Chem. - Eur. J.* **2013**, *19*, 13369–13375.

[3] P.-H. Xie, Y.-J. Hou, B.-W. Zhang, Y. Cao, F. Wu, W.-J. Tian, J.-C. Shen, *J. Chem. Soc. Dalton Trans.* **1999**, 4217–4221.
[4] W. A. Maza, S. R. Ahrenholtz, C. C. Epley, C. S. Day, A. J. Morris, *J. Phys. Chem. C* **2014**, *118*, 14200–14210.
[5] H.-P. Jing, C.-C. Wang, Y.-W. Zhang, P. Wang, R. Li, *RSC Adv* **2014**, *4*, 54454–54462.